SELECTIVE AND BLANKET ELECTROLESS Cu PLATING INITIATED BY CONTACT DISPLACEMENT FOR DEEP SUBMICRON VIA CONTACT FILLING

Valery M. Dubin, Yosi Shacham-Diamand
School of Electrical Engineering and National Nanofabrication Facility
Cornell University Ithaca, NY 14853
and
Bin Zhao, P.K. Vasudev, Chiu H. Ting
SEMATECH
2706 Montopolis Drive, Texas 78741-6499

ABSTRACT

Electroless Cu deposition for deep submicron via hole filling was performed after contact displacement activation of TiN diffusion barrier. Selective and blanket electroless Cu deposition processes have been developed. Contact displacement Cu deposition on TiN was performed in the activation solution containing Cu^{2+} cations and F^- anions as the main components. Various additives such as ammonium cyanide, 2,2'-dipyridyl, RE 610 and polyethylene glycols were studied in electroless Cu deposition solution to prevent spontaneous solution decomposition, to reduce the surface tension and to retard hydrogen inclusion in the deposit. The 0.35 µm Cu-filled vias with aspect ratio of ~ 4.3 were obtained by electroless Cu deposition on TiN diffusion layer after contact displacement activation. No voids/seams inside the subhalfmicron (down to 0.35 µm) electroless Cu plugs with very high aspect ratio (≥ 4) were observed.

INTRODUCTION

Copper are being considered as an alternative metallization material to Al alloys due to its low resistivity and ability to reliably carry high-current densities. The use of selective electroless Cu deposition process can simplify and reduce the cost of Cu metallization technology. Since the chlorides and fluorides of Cu are not volatile at room temperature, the use of anisotropic dry etching to pattern Cu films is very problematic. Two basic techniques can be used to achieve patterned electroless Cu films. a) Selective Cu deposition on base metal (diffusion barrier) into the trenches or vias in dielectric layer. b) Chemical-mechanical polishing following blanket Cu deposition onto diffusion barrier sputtered on patterned wafer containing vias and trenches in SiO_2.

The electroless deposition method involves the formation of a thin film of material from an electrolytic solution without external applied voltage. The deposition is due to an electrochemical reaction between the metal ions, reducing agent, complexing agents, and pH adjusters on a catalytic surface. Electroless metal deposition process can be divided into two step: anodic oxidation of reducing agents on catalytic metal surfaces and cathodic reduction of metal ions. Cu can be electrolessly deposited on the surface of Cu, Ni, Co, Au, Ag, Pd, Pt and Rh with formaldehyde as a reducing agent.

The role of catalytic materials in electroless Cu deposition process is to provide catalytic oxidation of reducing agents and to act as a conductive material for transport of electrons from the sites on the surface where anodic reaction occurs to the surface sites for

cathodic reduction of metal ions. Thus, electroless metal deposition process doesn't occur on dielectric surfaces and electroless plating is inherently selective.

TiN layer serves as a diffusion barrier in Cu-based metallization [1]. However, TiN is not catalytic material for electroless Cu deposition. Contact displacement activation of base metal (for example, TiN) is especially appealing technique because of low cost, process selectivity and compatibility with electroless Cu process. Metal ions from the solution simply displace surface atoms of base metal in contact displacement deposition reactions. Contact displacement Pd activation of base metals (TiN, TiW and Al) before selective electroless metal deposition was studied in works [2 - 4]. However, Pd acts as imperfection for electroless Cu film deposited on Pd-activated TiN layer. This leads to increase of Cu resistivity during subsequent annealing processes. In this work we study selective and blanket electroless Cu deposition for via hole filling following contact displacement Cu activation of TiN diffusion barrier.

EXPERIMENTAL

Selective electroless Cu deposition process was investigated for ULSI metallization structures containing the interconnection level (the 0.5 μm width Al-Cu/TiN lines), planarized interlevel dielectric (the 1.1 μm thick SiO_2 layer), 0.35 μm and 0.55 μm via holes in the interlevel dielectric. We also investigated blanket electroless Cu deposition on Ti(25nm)/TiN(40nm) layers deposited by collimated sputtering on patterned Si wafers with 0.35 μm and 0.50 μm vias which are about 1.5 μm deep. In both cases contact displacement Cu activation of TiN layer was used before electroless Cu deposition to fill the via holes.

Contact displacement deposition of Cu on TiN was performed at room temperature for 1 ÷ 600 sec in the activation solution containing Cu^{2+} cations and F^- anions as the main components (Table 1). An activation solution consists essentially of a soluble copper salt (supply of Cu^{2+} cations), such as copper sulfate, cupric chloride, cupric nitrate, copper gluconate, cupric acetate and supply of F^- anions such as hydrofluoric acid, ammonium fluoride etc.

Table 1. Composition of a copper activation solution.

COMPONENTS	CONCENTRATION
Cu^{2+} cations	0.001 - 1 mol/l
F^- anions	0.001 - 5 mol/l
Surfactant	0.01 - 0.1 g/l
DI H_2O	to 1 liter

Electroless Cu deposition solution contains copper sulfate (supply of Cu^{2+} cations), ethylenediaminetetraacetic acid (EDTA is the complexing agent for Cu^{2+} cations), potassium or quaternary ammonium (such as tetramethylammonium) hydroxides (supply of OH^-), formaldehyde or glyoxylic acid (reducing agent) and additives such as RE 610 or polyethylene glycols (surfactants and wetting agents), ammonium cyanide or 2,2'-dipyridyl (stabilizers and ductility promoters). Composition of electroless Cu deposition solution is presented in Table 2.

The amount of reducing agent and complexing agent are dependent up n the amount of cupric ions presented in the solution. Electroless Cu deposition reaction can be expressed as

$$2CH_2O + \{Cu[EDTA]\}^{2-} + 4OH^- \rightarrow Cu + H_2 + 2HCOO^- + 2H_2O + EDTA^{4-} \quad (1)$$

According to Eq. 1, the ratio between the components in the solution must be in molar as

$$1 \text{ mol } Cu^{2+} \; : \; 2 \text{ mol } CH_2O \; : \; 1 \text{ mol } EDTA^{4-} \quad (2)$$

Table 2. Electroless Cu bath composition and operation conditions.

COMPONENTS	CONCENTRATION
Copper sulfate	0.016 ÷ 0.08 mol/l
EDTA	0.04 ÷ 0.2 mol/l
Formaldehyde Glyoxylic acid	0.13 ÷ 1 mol/l 0.2 mol/l
Ammonium cyanide 2,2'-dipyridyl	0.01 mol/l 10 ÷ 120 ppm
Polyethylene glycol RE 610	50 ÷ 100 ppm 0.1 ÷ 1 g/l
Potassium/tetramethylammonium hydroxide (to adjust pH)	pH 11 ÷ 13
Temperature	30 ÷ 80 °C

The via hole filling capability of electroless Cu deposition process seeded by contact displacement deposition was investigated by SEM cross-sections. Focus ion beam (FIB) cross-sections were used to analyze void formation in electroless Cu-filled vias. The electrical resistivity of electroless Cu films was measured by four-point probe. The surface roughness and electrical uniformity of electroless Cu films were studied by Alpha-step® 200 and VersaProbe® VP10, respectively.

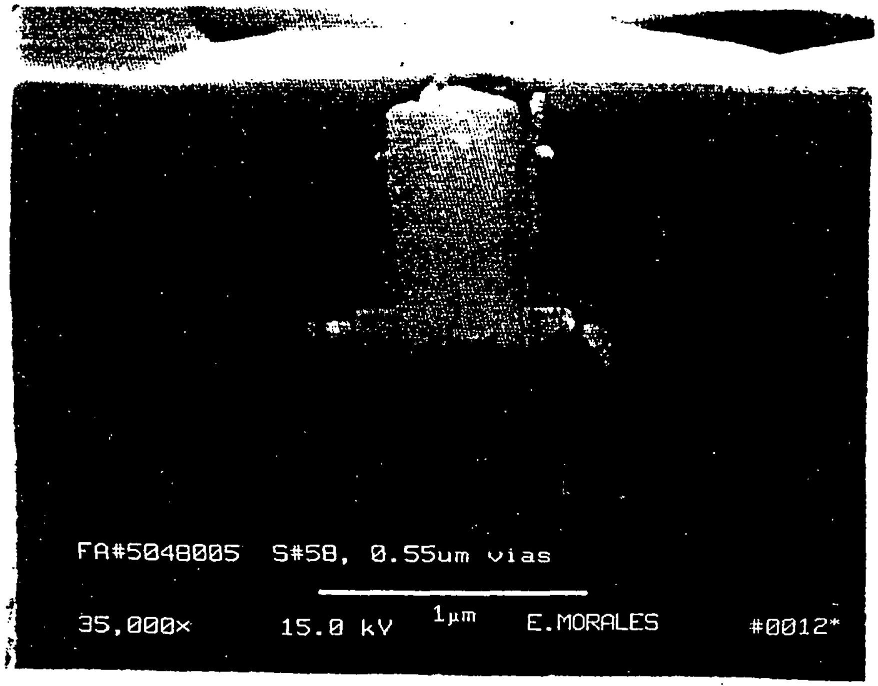
RESULTS AND DISCUSSION

Electroless Cu deposition solution was investigated in the range of concentrations described in Table 2. Solution composition was then optimized in order to obtain high deposition rate (120 ÷ 140 nm/min), low surface roughness ($R_a \leq 20$ nm), low resistivity (2 ÷ 2.1 $\mu\Omega$ cm) and good electrical uniformity ($\leq 5\%$) of electroless Cu films. The stability of electroless deposition solution was increased by using stabilizers such as cyanides and 2,2'-dipyridyl.

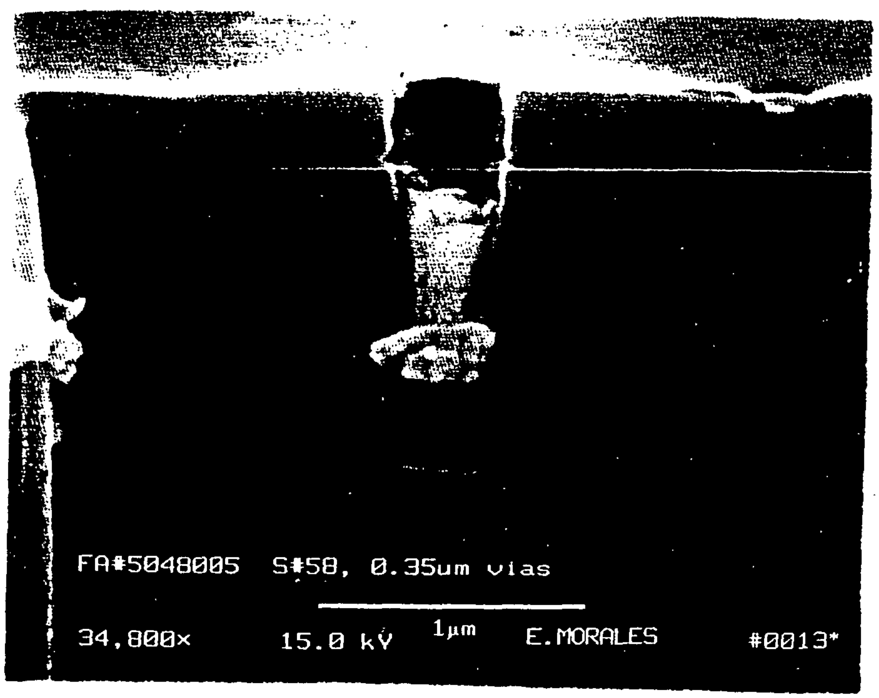
Selective Electroless Cu Plating on TiN Seeded by Contact Displacement. Process flow for selective electroless Cu deposition into via holes includes a) selective activation of base metal of lower metallization level (for example, AlCu/TiN) at the bottom of vias by contact displacement Cu deposition, b) selective electroless Cu deposition to fill the vias in interlevel dielectric layer, c) chemical-mechanical polishing to remove excess of Cu from overfilled vias.

It was observed that electroless Cu penetrates under interlevel dielectric layer. The penetration depth of Cu deposits depends on the interlevel dielectric being used and the concentrations of components in the activation solution. If, for example, SiO_2 is used as interlevel dielectric, Cu penetrates into SiO_2 - AlCu/TiN interface in depth of 10-100 nm (depends on the activation solution operation conditions). The penetration of Cu was also observed into interface of two SiO_2 layers if double-layer oxide was used as interlevel dielectric. This penetration of Cu into interface region increases the mechanical stability of metallization system. Fig. 1 shows electroless Cu plugs in the 0.55 μm via with aspect ratio of 2. The first interconnection level (AlCu/TiN) was selectively activated before electroless Cu plating by contact displacement Cu deposition for 10 sec at room temperature in the solution containing 200 g/l $CuSO_4$ $5H_2O$, 20 ml/l HF (48 %) and 0.1 g/l surfactant. The time of contact displacement deposition is crucial parameter for this process. Extensive etching of AlCu/TiN layer was observed when the time of contact displacement activation was 30 sec. No voids were found in electroless Cu-filled vias down to 0.35 μm via hole sizes with aspect ratio of ~3.

Fig. 1. Selective electroless Cu deposition into 0.55 μm via in 1.1 μm thick SiO_2 layer on Al(Cu-0.5%)/TiN conductor pattern activated by contact displacement Cu deposition.



a)



b)

Fig. 2. Selective electroless Cu deposition into via holes. a) The 0.55 μm Cu-filled via with aspect ratio of 2. b) The 0.35 μm Cu-filled via with aspect ratio of ~ 3. Notice: deposition rate of electroless Cu depends on via size.

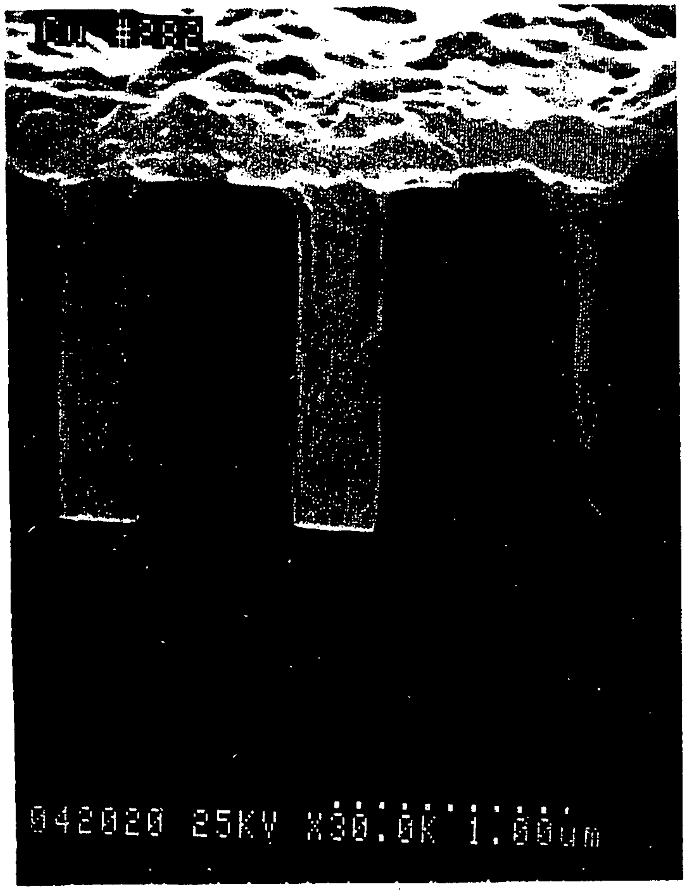


Fig. 3. The 0.35 μm vias with aspect ratio of ~4.3 filled by blanket electroless Cu deposition on collimated PVD Ti/TiN diffusion barrier activated by contact displacement Cu deposition

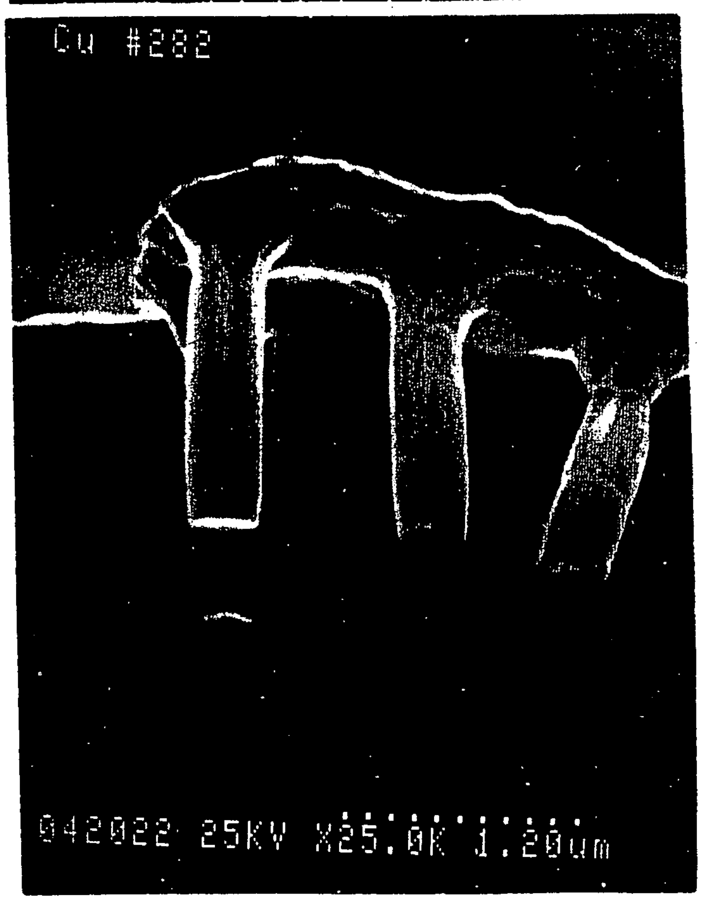


Fig. 4. The 0.35 μm electroless Cu plugs after dissolution of SiO_2 layer in diluted HF solution

Electroless Cu deposition rate into via holes depends mainly on the deposition temperature for the range of concentration of chemicals described in Table 2. The deposition rate increases with increasing solution temperature. The electroless Cu deposition rate up to 140 nm/min can be achieved at 75 °C. At this deposition rate the electroless Cu resistivity is still in the range of 2 ÷ 2.1 μΩ cm. Selective electroless Cu deposition rate into vias was also found to be via size dependent. For example, the thickness of electroless Cu deposits in the 0.35 μm vias with aspect ratio of 3 was ~ 30 % less than that in the 0.55 μm vias with aspect ratio of 2 (Fig. 2).

Blanket Electroless Cu Deposition on TiN Seeded by Contact Displacement. Selective electroless Cu deposition process described above allows to deposit voidless electroless Cu plugs into submicron vias (down to 0.35 μm) with high aspect ratio (up to 3). However, for this process there is no barrier layer on the side walls of vias. We develop the process of blanket electroless Cu deposition seeded by contact displacement Cu deposition to fill vias and to form electroless Cu plugs encapsulated with TiN diffusion barrier. Process flow consists in the following major steps: a) formation of vias in dielectric layer, b) collimated sputtering Ti/TiN diffusion barrier, c) contact displacement Cu deposition, d) electroless Cu deposition. Special treatments have to be done before and after contact displacement Cu activation of TiN diffusion barrier in order to increase adhesion of electrolessly deposited Cu films.

The 0.35 μm and 0.55 μm Cu vias with the 1.5 μm via depth were completely filled with electroless Cu by blanket electroless Cu deposition after contact displacement Cu deposition on Ti/TiN diffusion barrier. Fig. 3 shows the 0.35 μm Cu vias with aspect ratio of ~4.3 completely filled with electroless Cu using blanket electroless Cu deposition process on Ti(25 nm)/TiN(40 nm) diffusion barrier. No voids/seams were found in subhalfmicron electroless Cu-filled vias. The 0.35 μm electroless Cu plugs (wires) formed after dissolution of SiO_2 vias in diluted HF are depicted in Fig. 4. It can be seen from Fig. 4 that the subhalfmicron plugs (wires) are continuous, robust and without any voids.

CONCLUSIONS

Selective and blanket electroless Cu deposition processes on TiN diffusion barrier have been developed. Excellent filling the 0.35 μm size via holes with very high aspect ratios (up to ~ 4.3) was obtained by contact displacement activation of TiN with subsequent electroless Cu deposition. No voids/seams inside the Cu plugs were observed. No unfilled vias were found. Furthermore, the use of the same material for the seed layer (contact displacement deposited Cu) and plugs (electroless Cu) leads to low resistivity (lower than 2 μΩ cm) of electroless Cu deposits.

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